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4063 DTD/PM96009

2. Patent application number

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Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

U.S.A., New Jersey

4422242001

4. Title of the invention

Processes for Manufacture of  
Molecular Sieves

5. Name of your agent (if you have one)

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1 / 40

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## PROCESSES FOR MANUFACTURE OF MOLECULAR SIEVES

This invention relates to molecular sieves and processes  
5 for their manufacture. More especially it relates to  
processes in which synthesis mixtures are seeded to control  
process conditions and product characteristics. The  
invention relates primarily to the manufacture of zeolites  
and other crystalline molecular sieves. Examples of the  
10 latter include phosphorus-containing molecular sieves whether  
or not they have zeolite analogues.

It is well-known that seeding a molecular sieve  
synthesis mixture frequently has beneficial effects, for  
example in controlling the particle size of the product,  
15 avoiding the need for an organic template, accelerating  
synthesis, and improving the proportion of product that is of  
the intended structure type. Colloidal seeds, i.e., those  
with a particle size of at most about 400, especially at most  
300, preferably at most 200, and most preferably at most  
20 100 nm, have proved especially effective - see, for example,  
International Application Nos. WO 97/03019, 03020 and 03021,  
and EP-A-753483, 753484 and 753485.

Normally, the seeds used are of the same composition and  
structure type as the molecular sieve it is desired to  
25 produce although, when very small proportions of seeds are  
present as in the above-mentioned specifications and in  
WO 93/08124, it is possible to use seeds of the same  
structure type but of different composition. (When seeds of  
the same structure type are used, whether or not of the same  
30 composition, such seeding may be regarded as iso-structural.)  
On occasions, however, such seeds may not be available or may  
give undesirable results, while an unseeded mixture also  
gives undesirable results, as will be discussed in more  
detail below.

It has now surprisingly been found that seed crystals of a structure type different from that of the desired molecular sieve may be used with advantage in the manufacture of molecular sieves. Such seeding may be regarded as "hetero-  
5 structural".

As used in this specification, the term "structure type" is used in the sense described in the Structure Type Atlas, Zeolites 17, 1996.

The present invention accordingly provides in a first  
10 aspect a process for the manufacture of a crystalline molecular sieve, which comprises forming a synthesis mixture having a composition appropriate for formation of a molecular sieve of a first structure type and containing seed crystals of a second, different, structure type, and subjecting the  
15 seed-containing synthesis mixture to hydrothermal treatment for a time sufficient and at a temperature appropriate to form the desired molecular sieve.

In a second aspect, the invention provides the use, in the synthesis of a crystalline molecular sieve of a first  
20 structure type by hydrothermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a second, different, structure type to control the particle size of the product.

25 In a third aspect, the invention provides the use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a  
30 second, different, structure type to accelerate the formation of the product.

In a fourth aspect, the invention provides the use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis

mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a second, different, structure type to effect synthesis in the substantial absence of an organic template.

5        In a fifth aspect, the invention provides the use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a  
10 second, different, structure type to produce a product with enhanced phase purity.

         In a sixth aspect, the invention provides the use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis  
15 mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a second, different, structure type to direct the synthesis to the formation of a desired structure type.

         It was stated above that an unseeded synthesis mixture,  
20 or an iso-structurally seeded mixture, may give undesirable results. An example of this is given by a synthesis mixture suitable for producing a crystalline molecular sieve of the MFI structure type. This synthesis mixture is prone to yield a product in which many of the crystals are twinned. At the  
25 boundary or boundaries in twinned crystals, stacking faults exist which are such that they obstruct the pores through which molecules to be treated in some way, for example converted or separated, are to pass. This reduces the effectiveness of the molecular sieve, especially when the  
30 sieve is in the form of a layer, for example a membrane. It would therefore be of advantage if a molecular sieve of a structure type prone to yield twinned crystals could be made with a reduced incidence of twinning.

It has now unexpectedly been found that the inclusion of seeds of a second structure type in the synthesis mixture for a crystalline molecular sieve of a first structure type improves the crystallinity, more especially the internal  
5 crystallinity, of the product.

More especially, the presence of \*BEA seeds in an MFI structure type synthesis mixture will improve the crystallinity of the resulting MFI product.

Accordingly, in a seventh aspect, the invention provides  
10 the use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a second, different structure type to produce a  
15 product with improved crystallinity as shown by, for example, reduced twinning.

In an eighth aspect, the invention provides the use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis  
20 mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a second, different structure type to control the morphology of the product of the first structure type.

Examples of this aspect are the use of LEV seeds to give  
25 an OFF/ERI structure type, especially Linde Zeolite T, of disk-like morphology and OFF seeds to give the same material a needle-like morphology.

As molecular sieves to be prepared by the process of the first aspect of the invention, there may be mentioned more  
30 especially zeolites, aluminophosphates, and silicoaluminophosphates. As examples of structure types produced there may be mentioned more especially molecular sieves of the structure types MAZ, CHA, MOR, OFF, MFS, FER, TON, EUO and ERI/OFF and ZSM-48, not yet assigned a structure

type. As seeds, there may for example be used crystals of structure type LEV, OFF, MFI, \*BEA, MAZ, and CHA.

The seeds used in the present invention may be obtained by methods described herein or known in the art or described  
5 in the literature.

Apart from the presence of the seeds of different structure type, the synthesis mixture used in the present invention is in certain aspects of the invention one that is known in the art or as described in the literature as  
10 suitable for the production of the molecular sieve concerned except that the presence of the seeds may obviate the need for an organic template. This is also the case for the conditions of hydrothermal treatment, except that the presence of the seeds may make possible the reduction of  
15 reaction times or may obviate stirring if that were otherwise necessary.

However, in certain aspects of the invention, the presence of seeds of a second structure type will cause a synthesis mixture which in the absence of seeds would yield a  
20 crystalline molecular sieve of a third structure type to yield a crystalline molecular sieve of a desired first structure type.

More especially, the invention provides a process or use in which OFF structure type seeds are used in the manufacture  
25 of a crystalline molecular sieve of CHA structure type from a synthesis mixture which, if unseeded, would yield a crystalline molecular sieve of the FAU structure type.

In other aspects, the presence of seeds of a second structure type will cause a synthesis mixture which in the  
30 absence of seeds would not yield a crystalline molecular sieve at all (e.g., one that will produce only an amorphous product) to yield a crystalline molecular sieve of a desired first structure type.

In general, hydrothermal treatment is advantageously carried out under autogenous pressure, for example in an autoclave, for example a stainless steel autoclave which may, if desired, be ptfe-lined. The treatment may, for example, be  
5 carried out at a temperature within the range of from 50, advantageously from 90, especially 120, to 250°C, depending on the molecular sieve being made. The treatment may, for example, be carried out for a period within the range of from 20 to 200 hours, preferably from 50 to 100 hours, again  
10 depending on the molecular sieve being formed. The procedure may include an ageing period, either at room temperature or, preferably, at a moderately elevated temperature, before the hydrothermal treatment at more elevated temperature. The latter may include a period of gradual or stepwise variation  
15 in temperature.

For certain applications, the treatment is carried out with stirring or with rotating the vessel about a horizontal axis (tumbling). For other applications, static hydrothermal treatment is preferred. If desired, the  
20 synthesis mixture may be stirred or tumbled during an initial part of the heating stage, for example, from room temperature to an elevated, e.g., the final treatment, temperature, and be static for the remainder. Agitation generally produces a product with a smaller particle size and a narrower particle  
25 size distribution than static hydrothermal treatment.

The seeds are advantageously present in the synthesis mixture in a concentration of up to 2000, for example from 1 to 2000, preferably 100 to 1500, and more preferably 100 to 350, ppm, by weight, based on the total weight of the  
30 synthesis mixture. Although it is within the scope of the invention to use larger seeds, e.g., conventional powder seeds, the seeds are advantageously of particle size of at most 500 nm (in the case for example of needles or platelets, it is the smallest dimension that is referred to), as such

being regarded as near-colloidal, and preferably at most 400 nm, and more preferably of at most 100 nm, as such being regarded as colloidal. If the product is desired in small particle size form, a larger number of smaller sized seeds is  
5 desirably employed. Seeds may advantageously be added in the form of a suspension, advantageously in water or another constituent of the synthesis mixture, or they may less preferably be added in dried form.

More especially, the invention provides processes and  
10 uses in which LEV structure type seeds are used in the manufacture of a crystalline molecular sieve of the MFS structure type, for example ZSM-57, of the CHA structure type, for example chabazite, Linde D, Linde R, SSZ-13, SAPO-34, AlPO-34, MeAPO-34, MeAPSO-34, ELAPSO-34, or  
15 ELAPO-34, of the OFF structure type, for example offretite, of the MOR structure type, for example mordenite, of the MAZ structure type, for example mazzite, Zeolite omega, or ZSM-4, of the FER structure type, for example ferrierite, FU-9, ISI-6, NU-23, ZSM-21, ZSM-35 or ZSM-38, of the EUO structure  
20 type, for example EU-1, TPZ-3 or ZSM-50, or of the ERI/OFF structure type, for example zeolite Linde T or ZSM-34.

A stable suspension of LEV structure type crystals is novel; the invention accordingly further in a ninth aspect provides a suspension of a LEV structure type molecular  
25 sieve, the mean particle size of which is at most 100 nm.

The stable suspension of LEV may be obtained by synthesizing a LEV structure type molecular sieve by hydrothermal treatment of an appropriate synthesis mixture, and separating the product from the synthesis mixture,  
30 washing the product, and recovering the resulting wash liquid.

Examples of the LEV structure type include levyne, NU-3, ZK-20 and ZSM-45.

The invention further provides processes and uses in which OFF structure type seeds, especially offretite itself, are used in the manufacture of a crystalline molecular sieve of the CHA structure type, as exemplified above, of the MAZ structure type, as exemplified above, or of the MFS structure type, for example ZSM-57.

The invention further provides processes and uses in which MFI structure type seeds, for example silicalite, are used in the manufacture of a crystalline molecular sieve of the MOR structure type, for example mordenite.

The invention further provides processes and uses in which \*BEA structure type seeds, for example zeolite  $\beta$  or NU-2, are used in the manufacture of a ZSM-48 or EU-2 crystalline molecular sieve, or one of the MFI structure type, for example silicalite, or one of the EUO structure type, as exemplified above.

The invention further provides processes and uses in which MAZ structure type seeds, as exemplified above, are used in the manufacture of a crystalline molecular sieve of the OFF structure type, for example offretite.

The invention further provides processes and uses in which CHA structure type seeds, as exemplified above, are used in the manufacture of a crystalline molecular sieve of the OFF structure type, for example offretite.

In each case, advantageously the seeds used are of particle size (least dimension measured) at most 500 nm, preferably at most 400 nm, more preferably at most 200 nm and most preferably at most 100 nm.

The invention also provides the products of the processes and of the uses of the earlier aspects of the invention. The products, if required after cation exchange and/or calcining, have utility as catalyst precursors, catalysts, and separation and absorption media. They are especially useful in numerous hydrocarbon conversions,

separations and absorptions. They may be used alone, or in admixture with other molecular sieves, in particulate form, supported or unsupported, or in the form of a supported layer, for example in the form of a membrane, for example as described in WO 94/25151. Hydrocarbon conversions include, for example, cracking, reforming, hydrofining, aromatization, oligomerisation, isomerization, dewaxing, and hydrocracking (e.g., naphtha to light olefins, higher to lower molecular weight hydrocarbons, alkylation, transalkylation, disproportionation or isomerization of aromatics). Other conversions include the reaction of alcohols with olefins and the conversion of oxygenates to hydrocarbons.

The following Examples, in which parts are by weight unless otherwise indicated, illustrate the invention. The source and purity of starting materials are those first given, unless indicated otherwise.

#### Example 1

This example illustrates the manufacture of a LEV-type zeolite of particle size suitable for use as seeds in the manufacture, inter alia, of CHA, OFF, MAZ, FER, MFS, EUO and ERI/OFF structure types.

In a first stage, 15.95 parts of sodium aluminate (Dynamit Nobel, 53 %  $\text{Al}_2\text{O}_3$ , 41 %  $\text{Na}_2\text{O}$ , 6 %  $\text{H}_2\text{O}$ ), 19.95 parts of sodium hydroxide (Baker, 98.6 %) and 5.58 parts of potassium hydroxide (Baker, 87.4 %) were dissolved in 151.06 parts of water, and heated to boiling until a clear solution was obtained. After cooling to room temperature, water loss was compensated, to form Solution A. 270.60 parts of colloidal silica (Ludox HS40, 40 %  $\text{SiO}_2$ ) were mixed with 106.12 parts of choline chloride (R, Fluka) forming a viscous mass, and Solution A added with stirring at increasing speed as the viscosity decreased, together with 190 parts of rinse

water, mixing then continuing for a further 5 minutes. The molar composition was:

1.95 Na<sub>2</sub>O:0.24 K<sub>2</sub>O:0.46 Al<sub>2</sub>O<sub>3</sub>:10 SiO<sub>2</sub>:4.187 R:155 H<sub>2</sub>O.

5

To 290 parts of this mixture, 0.49 parts of conventional LEV zeolite seeds were added, and a sample transferred to an autoclave, where it was heated in a 120°C oven for 144 hours. The product was washed, recovered by centrifuging and dried  
10 overnight at 120°C. The product comprised spherical aggregates of from 2 to 2.5 µm, made up of ~100 nm particles, with an X-ray diffraction pattern (XRD) of ZSM-45, a zeolite of LEV-type structure, as described in EP-A-107 370 (Mobil).

The product was used as seeds in the next stage, in  
15 which 8.38 parts of sodium aluminate, 10.53 parts of sodium hydroxide, 2.96 parts of potassium hydroxide, and 78.95 parts of water were treated as described above to form a Solution A. Solution A was then added to a mixture of 142.42 parts of colloidal silica and 55.5 parts of choline chloride,  
20 together with 100.00 parts of rinse water and mixed as described above, with the addition of 0.68 parts of the first stage seeds. The reaction mixture was heated in an autoclave at 120°C for 174 hours, the product recovered by washing, centrifuging and drying having an XRD similar to  
25 that of the first stage. The second supernatant of the washing procedure was not clear, and had a pH of 10.3. It was found to be a dispersion with a solids content of 2.3 %. Analysis by scanning electron microscopy (SEM) and XRD showed ~100 nm crystals with a ZSM-45 structure, LEV structure type.

30

#### Example 2

This example illustrates the manufacture of a chabasite dispersion suitable for use, in turn, for seeding in

SAPO-34 manufacture by iso-structural seeding (not described). The seeds were prepared as follows:

A synthesis mixture was prepared as described in the first part of Example 1, except that as seeds the near-  
5 colloidal product from the second supernatant of the second part of Example 1 was used, at a seeding level of 0.15% by weight of solids. The seeded synthesis mixture was heated in a stainless steel autoclave for 96 hours at 120°C, with a heat-up time of 3 hours. The product, recovered by  
10 centrifuging and drying, had an XRD pattern corresponding to ZSM-45. The first supernatant was not clear and yielded, after centrifuging at 11000 rpm and further washing, a dispersion with solids content 4.6%, of crystals of size about 100 nm, XRD showing the product to be ZSM-45, a LEV  
15 structure-type zeolite.

Solution A was prepared as described in Example 1 using the following components, in the proportions shown:

	NaOH	61.66
20	KOH	28.73
	Al(OH) <sub>3</sub> (Alcoa, 99.3 %)	15.73
	H <sub>2</sub> O	190.30

300.23 parts of colloidal silica and 168.89 parts of  
25 water were poured into a mixer, and Solution A added together with 12.65 parts of rinse water. After mixing for 5 minutes, 16 parts of the 4.6 % solids LEV slurry were added. The molar composition of the synthesis mixture was:

30 3.8 Na<sub>2</sub>O:1.12 K<sub>2</sub>O:0.5 Al<sub>2</sub>O<sub>3</sub>:10 SiO<sub>2</sub>:161 H<sub>2</sub>O,  
with 927 ppm seeds.

The synthesis mixture was heated in an autoclave to 100°C over 2 hours, and maintained at that temperature for 96

hours. After cooling, the content of the autoclave, a milky suspension, was washed five times with demineralized water and centrifuged at 9000 rpm. After taking a sample for XRD and SEM, the remainder was redispersed to form a near-  
 5 colloidal solution, stable over several days, with a solids content of 6.4 %. The XRD of the product shows it to be chabasite, with a uniform particle size 100 x 400 nm.

### Example 3

10

This example illustrates the manufacture of SAPO-34 of small particle size and uniform size distribution.

A synthesis mixture was prepared from the following components in the proportions shown.

15

Solution	Component	Proportion
A	Al <sub>2</sub> O <sub>3</sub> (Pural SB Condea 75%)	68.18
	H <sub>2</sub> O	100.02
20 B	H <sub>3</sub> PO <sub>4</sub> (Acros, 85%)	115.52
	H <sub>2</sub> O,	80.27
C	Colloidal Silica (Ludox AS40)	22.73
	H <sub>2</sub> O, rinse	10.20
25 D	TEAOH (Eastern Chemical, 40%)	182.85
E	DPA (Fluka)	80.23
30 F	Seeds, 4.6 Wt.% LEV	31.95

Slurry A was prepared in a mixer, and Solution B added, when a viscous solution resulted. After leaving the solution to rest for 2 minutes, 26.84 parts of rinse water were added.

After mixing the paste for 6 minutes, C was added, and mixed for 2 minutes before adding Solution D. Upon adding E with 70.72 parts of rinse water two phases were formed. After a further 3 minutes mixing a visually homogeneous solution  
 5 resulted and after a further 10 minutes mixing the seeds F were added. The molar composition was:

$\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:0.3 \text{ SiO}_2:\text{TEAOH}:1.6 \text{ DPA}:56 \text{ H}_2\text{O}.$   
 + 1860 ppm by weight LEV seeds.

10

The seeded gel was heated for 60 hours at 175°C in a stainless steel autoclave. The solid product was recovered by centrifugation, washed 11 times with water to a conductivity of about 18  $\mu\text{S}/\text{cm}$ , and dried at 120°C. XRD and  
 15 SEM showed a pure SAPO-34 product with crystals between 0.2 and 1.3  $\mu\text{m}$ , with a few crystals between 2 and 3  $\mu\text{m}$ . Chemical analysis indicated a product of molar composition:

$\text{Al}_2\text{O}_3 : 0.99 \text{ P}_2\text{O}_5 : 0.36 \text{ SiO}_2.$

20

#### Example 4

This example illustrates the use of colloidal Offretite seeds in the manufacture of SAPO-34. The colloidal  
 25 Offretite was prepared as described in Example 2 of WO 97/03020. A synthesis mixture was prepared as described in Example 3, with the following molar composition:

$\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : 0.3 \text{ SiO}_2 : \text{TEAOH} : 1.6 \text{ DPA} : 51 \text{ H}_2\text{O}.$

30

To this was added a portion of a 5.36 % solids content colloidal offretite slurry (crystal size below 100 nm) to give a seeding level of 203 ppm. Hydrothermal treatment and product recovery were carried out as described in Example 5.

The product obtained was pure SAPO-34, the particle size of crystals being mainly between 0.2 and 1.3  $\mu\text{m}$ , with a few crystals between 2 and 3  $\mu\text{m}$  present.

5 Example 5

This example illustrates the use of powdered LEV, contaminated with some Offretite, in SAPO-34 manufacture. To the same synthesis mixture prepared for use in Example 4  
10 were added a LEV powder in a proportion to give a seed level of 217 ppm. The powder was mixed into the synthesis mixture gel by shaking the gel in a polypropylene bottle for 2 minutes. Hydrothermal treatment and product recovery were carried out as described in Example 4. The product was pure  
15 SAPO-34, with the majority of the crystals of size between 0.5 and 2.5  $\mu\text{m}$ .

Example 6

20 This example illustrates the use of colloidal LEV structure type seeds in manufacturing another non-LEV zeolite, in this case mordenite.

7.20 parts of NaOH, 26.90 parts of KOH (87.3%), 11.32 parts of  $\text{Al}(\text{OH})_3$  and 75 parts of water were boiled until a  
25 clear solution was obtained, cooled, and water added to compensate for the weight loss on boiling to provide solution A. 229.83 parts of Ludox AS40 were combined with 256.93 parts of water in a beaker, to which was added a solution of 68.70 parts of TEAOH in 100.02 parts of water. Finally  
30 solution A was added; rinse water totalling 25.41 parts was also added. A smooth gel resulted, of molar composition:

$^{-1.22}$  TEAOH:0.58  $\text{Na}_2\text{O}$ :1.37  $\text{K}_2\text{O}$ :0.47  $\text{Al}_2\text{O}_3$ :10  $\text{SiO}_2$ :235  $\text{H}_2\text{O}$ .

The synthesis mixture was divided, and to one sample, A, a colloidal LEV slurry, contaminated with some OFF, total solids content 4.6 % was added to give a seed level of 201 ppm. The other sample, B, remained unseeded.

5 Both synthesis mixtures were put into stainless steel autoclaves, and heated to 150°C over 2 hours. Sample A was maintained at that temperature for 96 hours, sample B was maintained at that temperature for 240 hours, with samples being taken at 48 and 96 hours.

10 After 96 hours, crystals had settled on the bottom of the autoclave containing sample A. XRD and SEM analysis of the product recovered showed MOR, with crystal sizes between 0.2 and 1.0  $\mu\text{m}$ , contaminated by a few OFF needles.

The 48 and 96 hours product samples from Sample B were  
15 amorphous; the 240 hours product contained MOR crystals of size range between 5 and 10  $\mu\text{m}$ , with amorphous material and OFF needles contamination. The Sample A product analysed:

$\text{SiO}_2 : \text{Al}_2\text{O}_3, 15.5 : 1.$

20

The sample shows that seeding with colloidal LEV accelerates the formation of mordenite and reduces the crystal size.

## 25 Example 7

This example further illustrates the use of LEV seeds in the manufacture of a non-LEV material, in this case ferrierite.

30 7.21 parts of NaOH, 26.92 parts of KOH, 11.31 parts of  $\text{Al}(\text{OH})_3$  and 75.02 parts of water were boiled until a clear solution was obtained, cooled, and water loss on boiling compensated to provide solution A. 229.87 parts of Ludox AS40 and 407.85 parts of water were poured into the beaker of

a mixer and solution A added, together with 14.18 parts of rinse water, and mixed for 10 minutes to provide a smooth gel synthesis mixture of the molar composition:

5        0.58 Na<sub>2</sub>O : 1.37 K<sub>2</sub>O : 0.47 Al<sub>2</sub>O<sub>3</sub> : 10 SiO<sub>2</sub> : 235 H<sub>2</sub>O.

The synthesis mixture was divided, and to one sample, A, the colloidal LEV slurry used in Example 6 was added to give a seed level of 207 ppm. The other part, Sample B, was  
10 unseeded. The samples were hydrothermally treated at the temperatures and times given in Example 6.

After 96 hours, crystals had settled on the bottom of the sample A autoclave. XRD and SEM analysis of the recovered product showed FER, in flake type crystals of about  
15 2 μm length, contaminated with OFF needles. Chemical analysis gave SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> of 15.6 : 1.

The 48 and 96 hours product samples from sample B were amorphous. After 240 hours, the sample B product contained FER crystals in admixture with amorphous material.

20        The examples show that organic template-free manufacture of ferrierite is accelerated by colloidal LEV crystals, and flake crystals result.

#### Examples 8 to 10

25

These examples illustrate the use of LEV colloidal seeds to make FER zeolite without the use of an organic template, and the effect of using two different seed concentrations. A template-free synthesis mixture of the following molar  
30 concentration was prepared:

2.16 K<sub>2</sub>O : 0.46 Al<sub>2</sub>O<sub>3</sub> : 10 SiO<sub>2</sub> : 157 H<sub>2</sub>O

and divided into three parts, samples A, B and C.

Sample A was unseeded.

Samples B and C (Examples 8 and 9) were seeded with a colloidal LEV seed slurry to levels of 260 ppm (Example 8) and 500 ppm (Example 9). Each sample was placed in a stainless steel autoclave, and heated at 200°C for 96 hours. Unseeded Sample A produced an amorphous product, while both Samples B and C produced the desired FER zeolite. The product of Sample C had a  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  molar ratio of 10 : 1. In a similar manner, a seeding level of 1000 ppm was used to produce, from a synthesis mixture (Example 10) having a molar composition of:

$2.16 \text{ K}_2\text{O} : 0.35 \text{ Al}_2\text{O}_3 : 10 \text{ SiO}_2 : 162 \text{ H}_2\text{O},$

a FER zeolite with a  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  molar ratio of 13 : 1.

#### Example 11

This example illustrates the use of colloidal LEV seeds to produce a different morphology of FER zeolite.

A synthesis mixture of the molar composition:

$0.45 \text{ Na}_2\text{O} : 3.1 \text{ pyridine} : 0.166 \text{ Al}_2\text{O}_3 : 10 \text{ SiO}_2 : 145 \text{ H}_2\text{O}$

was prepared and divided into two parts. One, Sample A, was seeded with sufficient 4.6 % LEV slurry to give a seed level of 224 ppm. The other part, Sample B, was left unseeded. Both samples were placed in a stainless steel autoclave and heated in two hours to 150°C and maintained at 150°C for 140 hours. The unseeded product was largely amorphous, with traces of ZSM-5. The LEV-seeded product was pure ZSM-35, a FER structure type zeolite, with a flat plate-like morphology.

Example 12

This example illustrates the effect of seeding level on particle size of FER.

5 A synthesis mixture similar to that of Example 1, first stage, was prepared, having a molar composition as follows:

1.95 Na<sub>2</sub>O : 0.23 K<sub>2</sub>O : 0.46 Al<sub>2</sub>O<sub>3</sub> : 10 SiO<sub>2</sub> : 4.15 choline chloride : 157 H<sub>2</sub>O.

This mixture was divided, to one sample, A, were added  
10 sufficient colloidal LEV seed slurry prepared as in Example 3 to give a seeding level of 200 ppm, while the other sample, B, had a seeding level of 600 ppm.

Each sample was heated at 150°C for 48 hours. The products, analysed by XRD and SEM, were identified as ZSM-38,  
15 a FER-type zeolite, as described in U.S. Patent No. 4 046 859. In both cases, the crystals were intergrown plates, with the crystal size depending on seeding level; 600 ppm giving a mean crystal size of 0.7 µm, while 200 ppm gave a mean crystal size of 1.0 µm.

20

Example 13

This example illustrates the use of colloidal LEV seeds to produce a Linde Zeolite T, of type structure ERI/OFF, and  
25 to control the morphology of the product.

The synthesis mixture used in Examples 8 to 10 was seeded with 200 ppm of the LEV slurry used there, and hydrothermal treatment carried out at 120°C instead of the 200°C used in those examples. The product was a disk-like  
30 crystallite of an intergrowth of ERI/OFF zeolite, known as Linde Zeolite T, as described in U.S. Patent No. 4 126 813.

Example 14

This example illustrates the control of particle size by seeding with LEV in the manufacture of a MAZ structure type zeolite. 32.38 parts of NaOH (98.6%) and 22.71 parts of  $\text{Al}(\text{OH})_3$  (98.5%) were dissolved in 63.37 parts of water by boiling, the solution cooled, and water loss compensated to form solution A. 17.60 parts of tetramethyl ammonium chloride (TMACl, 98%) were dissolved in 24.04 parts of water at room temperature in a high shear mixer and 218.78 parts of colloidal silica (Ludox HS-40, 40%) added with stirring over 2 minutes, then 5.38 parts of a 4.6% aqueous colloidal LEV solution, prepared as in Example 3, added and mixed for 3 minutes. Solution A was then added with 27.19 parts rinse water, and stirred in for 5 minutes, to give a paste-like gel with a molar composition of:

2.74  $\text{Na}_2\text{O}$ : 0.98  $\text{Al}_2\text{O}_3$ : 1.1 TMACl: 10 $\text{SiO}_2$ : 101  $\text{H}_2\text{O}$   
with 600 ppm LEV seeds.

20

380 parts of gel were heated in a plastic bottle fitted with a condenser in a 98°C oilbath for 135 hours. The resulting product was washed five times with 700 parts of water to a pH of 10.9, the product dried at 120°C (yield 89.5 parts) and calcined in air for 24 hours at 510 to remove the TMA, weight loss 9.2%. Product yield: 21.4%, XRD analysis showed an excellently crystalline TMA-MAZ and SEM showed uniform 500 nm spherical agglomerates consisting of nanocrystallites.

30

An unseeded but otherwise identical synthesis mixture subjected in the same hydrothermal treatment yielded a TMA-MAZ product slightly contaminated with TMA-sodalite, formed of spherical particles with a broad size distribution (about 0.3 to 2.5  $\mu\text{m}$ ).

Example 15

This example illustrates the control of particle size by seeding with colloidal OFF in the manufacture of a MAZ structure type zeolite.

Example 14 was repeated but using a colloidal OFF suspension, prepared as described in WO 97/03019, to give a synthesis mixture of molar composition:

2.74 Na<sub>2</sub>O: 0.99 Al<sub>2</sub>O<sub>3</sub>: 1.1 TMACl: 10SiO<sub>2</sub>: 101 H<sub>2</sub>O  
with 600 ppm OFF seeds.

The product was excellently crystalline TMA-MAZ consisting of 0.2 to 0.3  $\mu$ m agglomerates of 30 to 50 nm crystallites.

Example 16

This example illustrates how seeding, with colloidal OFF, directs a zeolite Y synthesis mixture to yield a CHA structure zeolite.

A synthesis mixture was prepared following the procedure described in Example 14, but of molar composition:

2.74 Na<sub>2</sub>O: 0.99 Al<sub>2</sub>O<sub>3</sub>: 10SiO<sub>2</sub>: 101 H<sub>2</sub>O.

One sample of the synthesis mixture was seeded with 630 ppm colloidal OFF seeds, the other remained unseeded. Both samples were aged for 67.5 hours then heated in a 98°C oilbath, the seeded sample for 192 hours, the unseeded one for 172.5 hours.

The seeded sample mother liquor was unclear after heating, indicating very small crystallite formation; XRD analysis of the product showed a diffuse chabasite pattern,

shown by SEM to be sub-micron agglomerates of nano-sized crystallites. The comparative, unseeded, sample consisted of zeolite Y (structure type FAU).

5 Example 17

This example illustrates the effect of colloidal MFI seeds in mordenite synthesis.

Following the procedure described in Example 14, a  
10 synthesis mixture was prepared with a molar composition as follows:

2.60 K<sub>2</sub>O: 0.30 Al<sub>2</sub>O<sub>3</sub>: 10SiO<sub>2</sub>: 201 H<sub>2</sub>O

15 One sample of the mixture was unseeded and a second seeded with a colloidal silicalite suspension (prepared as in WO 93/08125) to give a 610 ppm seeding level. The samples in autoclaves were heated to 160°C in an oven. After both 130 and 260 hours the unseeded sample yielded an amorphous  
20 product. The seeded sample was heated for 202 hours, and the resulting product was excellently crystalline mordenite. TGA showed the product to be large port mordenite (7.53% toluene absorbed after 60 minutes desorption with N<sub>2</sub>).

25 Examples 18 and 19

These examples illustrate particle size control of zeolite ZSM-48 using colloidal  $\beta$  seeds.

The seeds were prepared by forming a synthesis mixture  
30 of the following molar composition using tetraethylammomium hydroxide (TEAOH) as template:

-2.78 (TEA)<sub>2</sub>O: 0.22 Al<sub>2</sub>O<sub>3</sub>: 10SiO<sub>2</sub>: 79H<sub>2</sub>O

The mixture, in a condenser-equipped plastic bottle, was heated for 37 days in a 70°C oilbath to give a slurry of solids content 16.64%. The product was centrifuged, washed with water, and the precipitate redispersed to give a 0.5% aqueous seed dispersion.

A synthesis mixture was prepared using 1,6-diaminohexane (R, 97%) as template and Ludox AS-40 as the colloidal silica source. The molar composition was:

0.71 Na<sub>2</sub>O: 3.04R: 10SiO<sub>2</sub>: 377 H<sub>2</sub>O

One sample (Example 18) of the mixture was seeded with the colloidal  $\beta$  suspension to a seeding level of 0.105% and the other (Example 19) to a level of 50 ppm. The samples were heated in autoclaves in a 150°C oven for 20 hours. The products were washed with water to pH of 9.5, dried at 120°C and calcined for 20 hours at 510°C. Both products were excellently crystalline pure ZSM-48. The Example 18 material was intergrown rice-like particles of about 0.4  $\mu$ m length, which in turn consisted of crystallites of between 50 and 125 nm. The product of Example 19 had a particle size of about 1.0  $\mu$ m.

In a comparative example, the same synthesis mixture, seeded with 174 ppm of powdered ZSM-48, was hydrothermally treated at 150°C for 40 hours. The product, washed to a pH of 10.1 and dried at 120°C, was excellently crystalline pure ZSM-48, in the form of rice-like particles between 4 and 5  $\mu$ m long, with no twinning.

Example 20

This example illustrates particle size control of offretite using near-colloidal TMA-MAZ seeds prepared in a way similar to those prepared in Example 3.

A synthesis mixture was prepared, using TMACl as the template and Ludox HS40 as colloidal silica source. The molar composition was:

2.2 K<sub>2</sub>O: 1.00 TMACl: 1.0 Al<sub>2</sub>O<sub>3</sub>: 10SiO<sub>2</sub>: 163 H<sub>2</sub>O

One sample was left unseeded, and another seeded with a near-colloidal 0.43% solids suspension of TMA-MAZ to a level of 600 ppm. Each was placed in an autoclave and maintained at 150°C for 48 hours. The seeded sample produced of 1.0 to 1.5 µm crystallites of pure OFF. The unseeded sample consisted of OFF slightly contaminated by zeolites K-L and W. The crystals were significantly larger, with a broader size distribution (3 to 6 µm).

Examples 21 and 22

These examples illustrate the use of colloidal LEV and near-colloidal CHA seeds in controlling the particle size of offretite.

A synthesis mixture was prepared using TMACl as the template and Ludox AS40 as silica source. The molar composition was:

2.3 K<sub>2</sub>O: TMACl: Al<sub>2</sub>O<sub>3</sub>: 10SiO<sub>2</sub>: 160 H<sub>2</sub>O.

One sample (Example 21) was seeded to a level of 202 ppm using a 4.6% solids content dispersion of colloidal LEV (see Example 3). The mixture was heated in an autoclave at 150°C

for 8 hours. The product was pure OFF, with crystals having a narrow size distribution, about 1  $\mu\text{m}$ .

Another sample (Example 22) was seeded to a level of 310 ppm using an 11% solids content of near colloidal CHA,  
5 prepared as described in Example 2. The mixture was heated in an autoclave at 150°C for 24 hours. The product was pure OFF, with crystals of about 3  $\mu\text{m}$ .

A further sample was left unseeded, and heated for 150°C for 48 hours. The product was pure OFF, with particle sizes  
10 ranging between 1 and 5  $\mu\text{m}$ .

#### Examples 23 and 24

These Examples illustrate the use of colloidal OFF and  
15 LEV seeds to control purity and particle size in ZSM-57 manufacture.

A synthesis mixture was prepared using N,N,N,N',N',N' hexaethylpentane diammonium bromide (R) as template, Ludox HS 40 as silica source, and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  as alumina source.  
20 The molar composition was:

R:  $2\text{Na}_2\text{O}$ : 0.17  $\text{Al}_2\text{O}_3$ : 10 $\text{SiO}_2$ : 399.4  $\text{H}_2\text{O}$

A first sample (Example 23) seeded with colloidal OFF to  
25 a level of 221 ppm was heated at 160°C in an autoclave. After 144 hours the product was still XRD amorphous but by 196 hours pure ZSM-57 was recovered; crystal morphology was platelets, 200 nm to 2  $\mu\text{m}$ .

A second sample (Example 24) seeded with 175 ppm  
30 colloidal LEV was heated at 160°C for 144 hours. The product was fully crystalline ZSM-57, with particle size about 1  $\mu\text{m}$ .

A third sample was left unseeded, and heated at 160°C. Crystallization did not start until 14 days. After 24 days

the product was a mixture of ZSM-57, quartz and other crystalline phases, the ZSM-57 material was platelets of about 3  $\mu\text{m}$  diameter, mixed with other crystallites.

5 Examples 25 and 26

These Examples illustrate the use of colloidal LEV seeds in the manufacture of a FER type zeolite, ZSM-38.

A synthesis mixture was prepared using sodium aluminate  
10 (Nobel, 53%  $\text{Al}_2\text{O}_3$ , 41%  $\text{Na}_2\text{O}$ ) as the alumina source, Ludox HS 40 as the silica source and choline chloride (R, Aldrich) as template. The mixture had the molar composition:

1.95  $\text{Na}_2\text{O}$ : 0.24  $\text{K}_2\text{O}$ : 0.46  $\text{Al}_2\text{O}_3$ : 10 $\text{SiO}_2$ : 4.17R: 157  $\text{H}_2\text{O}$   
15

One sample was used unseeded, a second (Example 25) was seeded with a 4.6% solids content slurry of near-colloidal LEV to a 200 ppm loading. Both samples were heated in autoclaves at 150°C. After 71 hours the unseeded sample was  
20 still amorphous. After 48 hours, the seeded sample had produced ZSM-38, an FER structure type zeolite (see U.S. Patent No. 4 046 859), crystal size (intergrown plates) about 1.0  $\mu\text{m}$ .

A third sample (Example 26) was similarly seeded but to  
25 a loading of 0.06%. After being similarly heated, the product was similar to that of Example 25, but the crystal size was smaller, at about 0.7  $\mu\text{m}$ .

Example 27

30

In this example colloidal OFF seeds are used in the manufacture of an ERI/OFF structure type zeolite, and to control the morphology of the product.

A synthesis mixture was formed using Ludox HS 40 as silica source and choline chloride (R) as template. The molar composition was:

5        2.16 K<sub>2</sub>O: 4.17R 0.46 Al<sub>2</sub>O<sub>3</sub>: 10SiO<sub>2</sub>: 157 H<sub>2</sub>O.

One sample was left unseeded, the other was given a 0.02% loading of OFF seeds. Both samples were heated in an autoclave for 96 hours at 120°C. The product of the unseeded  
10 mixture was amorphous, the seeded mixture yielded needle-like crystals of zeolite T, an intergrowth of ERI and OFF zeolite, as described in U.S. Patent No. 4 116 813.

#### Example 28

15

This example illustrates the improvement in crystallinity resulting from heterostructural seeding.

A synthesis mixture was prepared from 2.99 parts of NaOH (98.6%), 450.88 parts of demineralized water, 23.26 parts of  
20 tetrapropylammonium bromide (TPABr) and 249.27 parts of silica gel (Ludox HS-40), to give a mixture of molar composition:

0.23 Na<sub>2</sub>O : 0.53 TPABr : 10SiO<sub>2</sub> : 201 H<sub>2</sub>O

25

To 51.5 parts of the synthesis mixture were added 1.74 parts of a slurry containing 16.64% solids of \*BEA crystals, of 80 nm particle size, to give a seed concentration of 0.56%. The seeded mixture was heated during 30 minutes in a  
30 polypropylene bottle to 90°C, and maintained at that temperature for 36 hours. The solid product resulting was washed, and dried overnight at 120°C. XRD of the dried product showed that it was mainly MFI with some \*BEA present. SEM showed two morphologies: spherical crystals of \*BEA or

MFI, about 100 nm, and flat MFI crystals ranging from 100 to 700 nm, with practically no twinning.

By way of comparison, an unseeded synthesis mixture and synthesis mixtures seeded with either spherical MFI crystals (49 ppm, 50 nm diameter) or flat MFI crystals (53 ppm, about 200 nm in the smallest dimension) were subjected to hydrothermal treatment.

The unseeded mixture produced no crystals after 36 hours at 90°C; heating at 90°C for a further 108 hours produced a very low yield of crystals. SEM showed a very broad size distribution, from 1 to 5  $\mu\text{m}$ , with the smaller crystals mainly untwinned but those larger than 2  $\mu\text{m}$  all twinned.

The MFI seeded mixtures both produced MFI after 36 hours at 90°C. The mixture seeded with 50 nm spherical seeds produced a largely twinned product of a crystal size between 0.5 and 1.5  $\mu\text{m}$ . The "flat" seeded mixture gave MFI crystals between 1 and 2  $\mu\text{m}$  with slightly less twinning than the spherically seeded mixture, but still substantially more than that seeded by \*BEA.

The colloidal \*BEA seeds used in this example were prepared using the procedure described in Examples 18 and 19, using the product of hydrothermal treatment at its original concentration.

## Example 29

This example illustrates the effect of colloidal LEV and colloidal \*BEA in the synthesis of ZSM-50 (structure type EUO). The use of colloidal LEV reduces the crystallization time needed under static condition compared to a synthesis mixture seeded with colloidal \*BEA.

A solution A was prepared using the following ingredients in the proportions indicated:

28

$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	18.98
NaOH (98.7%)	27.59
$\text{H}_2\text{O}$	150.06

5        225.06 parts of colloidal silica (Ludox HS40) and 765.01  
parts of water were poured together and mixed. Solution A  
was added using 21.38 parts of rinse water. After mixing,  
solution B, consisting 61.57 parts of hexamethonium bromide  
(R) in 100.49 parts of water was added using 20.82 parts of  
10 rinse water. To 798.64 parts of the mixture which was  
homogenized were added 3.032 parts of the 4.6 Wt.% colloidal  
slurry of LEV of Example 3. The final homogeneous mixture  
with the following molar composition:

15         $2\text{Na}_2\text{O/R/0.17Al}_2\text{O}_3/10\text{SiO}_2/401 \text{ H}_2\text{O} + 174 \text{ wtppm LEV}$

was transferred to a 1 litre stainless steel autoclave and  
heated to 150°C over 6 hours. Heating was continued for 168  
hours. The sample was washed and dried and XRD and SEM  
20 showed ZSM-50, elliptical plates of length 1 $\mu\text{m}$ .

A mixture with composition

$2\text{Na}_2\text{O/R/0.17Al}_2\text{O}_3/10\text{SiO}_2/401 \text{ H}_2\text{O} + 142 \text{ wtppm *BEA}$

25 was prepared and crystallized in the same way as above. A  
sample was taken after 168 hours of heating at 150°C. XRD  
showed very poor crystallinity. After 216 hours of heating  
the crystallinity of the recovered product increased. The  
product was fully crystalline ZSM-50 after 312 hours.

CLAIMS

1. A process for the manufacture of a crystalline molecular sieve, which comprises forming a synthesis mixture having a composition appropriate for formation of a molecular sieve of a first structure type and containing seed crystals of a second, different, structure type, and subjecting the seed-containing synthesis mixture to hydrothermal treatment for a time sufficient and at a temperature appropriate to form the desired molecular sieve.
2. The use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a second, different, structure type to control the particle size of the product.
3. The use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a second, different, structure type to accelerate the formation of the product.
4. The use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a second, different, structure type to effect synthesis in the substantial absence of an organic template.
5. The use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of

a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular sieve of a second, different, structure type to produce a product with enhanced phase purity.

5

6. The use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular  
10 sieve of a second, different, structure type to direct the synthesis to the formation of a desired structure type.

7. The invention as claimed in any of claims 1 to 6, wherein the first structure type is MAZ, CHA, MOR, OFF, MFS,  
15 FER, ERI/OFF, TON, EUO or the zeolite is ZSM-48.

8. The invention as claimed in any one of claims 1 to 7 wherein the second structure type, being different from the first, is LEV, OFF, MFI, \*BEA, MAZ, or CHA.

20

9. A process for the manufacture of a crystalline molecular sieve of a first structure type, which comprises forming a synthesis mixture having a composition appropriate for formation of a molecular sieve of a third structure type and  
25 containing seed crystals of a second structure type, and subjecting the seed-containing synthesis mixture to hydrothermal treatment for a time and temperature sufficient for the formation of the first structure type molecular sieve, the first, second and third structure types being  
30 different from each other.

10. A process as claimed in claim 9, wherein the first, second and third structure types are CHA, OFF, and FAU respectively.

11. The invention as claimed in any one of claims 1 to 6, in which LEV structure type seeds are used in the manufacture of a crystalline molecular sieve of the MFI structure type, of the CHA structure type, of the OFF structure type, of the MOR structure type, of the FER structure type, of the EUO structure type, or of the ERI/OFF structure type.

12. The invention as claimed in any one of claims 1 to 6, in which OFF structure type seeds are used in the manufacture of a crystalline molecular sieve of the CHA structure type, of the MAZ structure type, or of the MFI structure type.

13. The invention as claimed in any one of claims 1 to 6, in which MFI structure type seeds are used in the manufacture of a crystalline molecular sieve of the MOR structure type.

14. The invention as claimed in any one of claims 1 to 6, in which \*BEA structure type seeds are used in the manufacture of a crystalline molecular sieve of the EUO structure type, or of the MFS structure type, or the zeolite ZSM-48.

15. The invention as claimed in any one of claims 1 to 6, in which MAZ structure type seeds are used in the manufacture of a crystalline molecular sieve of the OFF structure type.

16. The invention as claimed in any one of claims 1 to 6, in which CHA structure type seeds are used in the manufacture of a crystalline molecular sieve of the OFF structure type.

30

17. The use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular

sieve of a second, different structure type to produce a product with improved crystallinity.

18. The use as claimed in claim 17 wherein improved  
5 crystallinity is shown by reduced twinning.

19. The use as claimed in claim 17 or claim 18, wherein the first structure type is MFI and the second structure type is \*BEA.

10

20. The use, in the synthesis of a crystalline molecular sieve of a first structure type by hydrothermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of seed crystals of a crystalline molecular  
15 sieve of a second, different structure type to control the morphology of the product of the first structure type.

21. The use as claimed in claim 20, wherein LEV seeds are used to form Linde Zeolite T of disk-like morphology.

20

22. The use as claimed in claim 20, wherein OFF seeds are used to form Linde Zeolite T of needle-like morphology.

23. The invention as claimed in any preceding claim, wherein  
25 the seeds used are of particle size (least dimension measured) at most 500 nm, preferably at most 400 nm, and most preferably at most 100 nm.

24. A suspension of a LEV structure type molecular sieve,  
30 the mean particle size of which is at most 100 nm.

25. The invention as claimed in claim 1 or claim 9, carried out substantially as described in any one of the Examples herein.

26. A molecular sieve whenever produced by an invention as claimed in any preceding claim.

5 27. A molecular sieve as claimed in claim 26 in particulate or layer form.

28. The use of the product as claimed in claim 26 or claim 27 if desired after washing, cation exchange, or calcining,  
10 in hydrocarbon conversion, adsorption, or separation.

29. Any new feature or new combination of features herein described.

## ABSTRACT

## 5                    PROCESSES FOR MANUFACTURE OF MOLECULAR SIEVES

                  The manufacture of a crystalline molecular sieve of a  
                  given structure type using seeds of a different structure  
10 type.